

NPS ARCHIVE
1968
MONK, W.

KINETICS OF AMMONIA SUBSTITUTION INTO
TETRACHLOROPALLADATE (II) ION

WILLIAM WADE MONK

DUDLEY KNOX LIBRARY
NAVAL POSTGRADUATE SCHOOL
MONTEREY CA 93943-5101

KINETICS OF AMMONIA SUBSTITUTION INTO
TETRACHLOROPALLADATE (II) ION

By

William Wade Monk
Lieutenant, United States Navy
B.A., Texas College of Arts and Industries, 1957



Submitted in partial fulfillment of the
requirements for the degree of

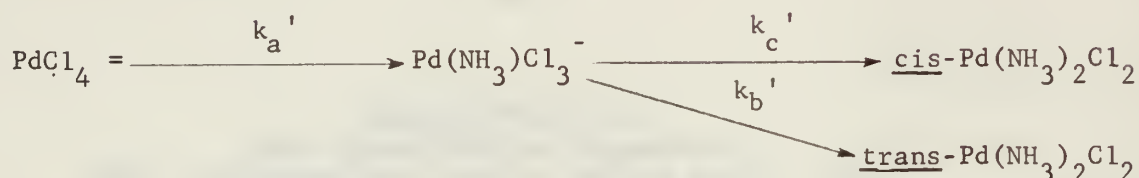
MASTER OF SCIENCE IN CHEMISTRY

from the

NAVAL POSTGRADUATE SCHOOL
June 1968

ABSTRACT

The kinetics of ammonia substitution into tetrachloropalladate (II) ion were studied by ultraviolet spectroscopy. The reactions in aqueous solution follow the course



Each pseudo-first-order rate constant was found to obey the two-term rate law.

$$k' = k_1 \frac{(\text{NH}_3)}{(\text{Cl}^-)} + k_2 (\text{NH}_3)$$

indicating a dual-path mechanism involving solvent substitution.

Values found at 30°C and $\mu = 1$ are $k_{a1} = 89.8 \text{ sec}^{-1}$, $k_{a2} = 31.3 \text{ M}^{-1} \text{ sec}^{-1}$, $k_{b1} = 12.5 \text{ sec}^{-1}$, and $k_{b2} = 6.5 \text{ M}^{-1} \text{ sec}^{-1}$. Values estimated for the rapid step leading to cis-Pd(NH₃)₂Cl₂ are $k_{c1} = 630 \text{ sec}^{-1}$ and $k_{c2} = 220 \text{ M}^{-1} \text{ sec}^{-1}$.

Activation parameters of the first step are calculated.

The trans and cis effects are discussed.

Table of Contents

Section		Page
I	Introduction	11
II	Mechanism and Effects	12
III	Mathematical Models of Kinetics	16
IV	Experimental Methods	25
V	Data Handling and Results	32
VI	Discussion	40
	Bibliography	43
	Appendix A	44
	Appendix B	57

List of Tables

Table		Page
3-1	Molar Absorptivities of $\text{PdCl}_4^{=}$ in <u>3M</u> HCl	22
3-2	Molar Absorptivities of the chloroammine complexes of palladium	23
4-1	Run solution composition	31
5-1	Palladium independence results	32
5-2	Acetate independence results	34

List of Illustrations

Figure		Page
3-1	Plot of $\ln(D - D_{\infty})$ versus time	20
3-2	Plot of $\ln \Delta$ versus time	21
4-1	Atomic absorption reference plot	30
5-1	Program KINET output plot	33
5-2	Plot of $\frac{k_{\text{obsd}}}{[\text{NH}_3]}$ versus $\frac{1}{[\text{Cl}^-]}$ for first step data at 25°C	35
5-3	Plot of $\frac{k_{\text{obsd}}}{[\text{NH}_3]}$ versus $\frac{1}{[\text{Cl}^-]}$ for first step data at 30°C	36
5-4	Plot of $\frac{k_{\text{obsd}}}{[\text{NH}_3]}$ versus $\frac{1}{[\text{Cl}^-]}$ for second step data at 30°C	38

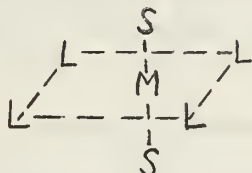
Table of Symbols

Symbol	Definition
Pd4	$\text{PdCl}_4^{=}$
Pd3	$\text{Pd}(\text{NH}_3)\text{Cl}_3^{-}$
<u>cis</u> -Pd2	<u>cis</u> - $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$
<u>trans</u> -Pd2	<u>trans</u> - $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$
D	Absorbance
ϵ_A	Molar absorptivity of $\text{PdCl}_4^{=}$
ϵ_B	Molar absorptivity of $\text{Pd}(\text{NH}_3)\text{Cl}_3^{-}$
ϵ_C	Molar absorptivity of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$
k_B	Boltzmann constant

SECTION I

INTRODUCTION

Palladium is a transition element, lying vertically between Ni and Pt in the periodic table. Like Pt and Ni, it forms square planar complexes in the +2 state. Current theory is that the square planar configuration is a tetragonally distorted octahedron of the type:



where the S ligands are solvent molecules or other species present and are loosely held at the apices.

The chloroammine series of complexes is comprised of six complexes: $\text{PdCl}_4^{=}$; $\text{PdCl}_3(\text{NH}_3)^{-}$; $\text{PdCl}_2(\text{NH}_3)_2$ (which exists in both cis and trans isomers); $\text{PdCl}(\text{NH}_3)_3^{+}$; and $\text{Pd}(\text{NH}_3)_4^{++}$. The kinetics and equilibria of the ammonia-rich species as well as the kinetics of Cl^{-} substitution into $\text{PdCl}_2(\text{NH}_3)_2$ and $\text{PdCl}_3(\text{NH}_3)^{-}$ have been reported^{1,2,3}. The chloride-rich equilibria are unknown, however, as is the cis-trans equilibrium of $\text{PdCl}_2(\text{NH}_3)_2$. When NH_3 is added to a solution of $\text{PdCl}_4^{=}$, a rapid substitution reaction occurs, initially forming $\text{PdCl}_2(\text{NH}_3)_2$, then continuing more slowly to ultimately form $\text{Pd}(\text{NH}_3)_4^{++}$. The kinetics of the first two substitutions of Cl^{-} by NH_3 is the main topic of this thesis.

¹) R. A. Reinhardt, N. L. Brenner, and R. K. Sparkes, Inorg. Chem., 6, 254 (1967)

²) R. A. Reinhardt and R. K. Sparkes, ibid, 6, 2190, (1967)

³) A. J. Poe and D. H. Vaughn, Inorg. Chim. Acta, 1, 255 (1967)

SECTION II

MECHANISM AND EFFECTS

STERIC MODEL

The square-planar geometry is well suited for substitution by associative pathways since there are two coordination positions open for attack by an entering group. From a purely steric consideration, the transition state or intermediate (which is five-coordinated) is expected to have a trigonal-bipyramidal geometry, as shown in Figure 2-1. This form allows minimum mutual electrostatic repulsion of the ligands and, in addition, allows each ligand maximum room.

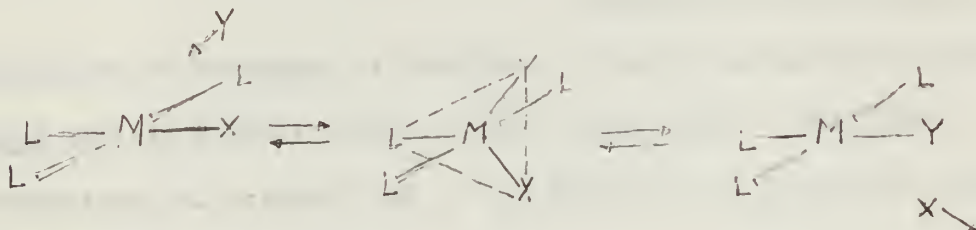


Figure 2-1: Square-planar substitution via a trigonal-bipyramidal transition state.

RATE LAW

It is generally recognized⁴ that most square-planar substitutions follow a two-term rate law of the form:

$$-\frac{d(\text{Complex})}{dt} = \{k_1 + k_2(Y)\} (\text{Complex})$$

where k_1 and k_2 are first and second order rate constants respectively, and (Y) is the concentration of the entering ligand. The second order term follows directly from the proposals in the preceeding section, but the first order term indicates the existence of another pathway.

⁴) F. Basolo and R. G. Pearson, Mechanisms of Inorganic Reactions, 2nd Ed., J. Wiley and Sons, Inc., New York, 1967, pp. 377-378

If a mechanism is postulated involving replacement of the leaving group by a solvent molecule with consequent rapid elimination by the entering group, the rate law can be re-written as:

$$-\frac{d(\text{Complex})}{dt} = \{k_s (S) + k_2 (Y)\} (\text{Complex})$$

where $k_1 = k_s (S)$. If, however, the rate-determining step in the solvent pathway is the solvent replacement by the entering group, the rate law becomes:

$$-\frac{d(\text{Complex})}{dt} = \left\{ \frac{k_1(Y)}{(X)} + k_2 (Y) \right\} (\text{Complex})$$

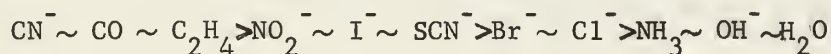
where (X) is the concentration of the leaving group.

The foregoing discussion has been concerned only with the entering and leaving groups. Other ligands in the complex, however, may affect the values of either or both rate constants although they do not appear explicitly in the rate law.

TRANS EFFECT

Basolo and Pearson⁵ have defined the trans effect as the effect of a coordinated group upon the rate of substitution reactions of ligands opposite to it in a metal complex. This is generally considered an accelerating effect and will be defined as such here.

Although the trans effect of ligands undoubtedly varies with the substrate, the generally accepted "average" order is



Two distinct, but not mutually exclusive theories have been suggested to explain the trans effect⁶. One, the electrostatic polarization

⁵) F. Basolo and R. G. Pearson, ibid, p. 356

⁶) C. H. Langford and H. B. Gray, Ligand Substitution Processes, W. A. Benjamin, Inc., New York, 1966, pp. 25-29

theory explains the effect in terms of p orbital distortion by the trans ligand. Since the trans group and the leaving group share the same p orbital, a group with a particularly strong σ interaction with the orbital may weaken the bond to the leaving group. The leaving group then moves out of direct alignment as it "seeks" more orbital overlap with adjacent p orbitals. This allows the entering group to move in as shown in Figure 2-2 to form the trigonal-bipyramidal transition state.

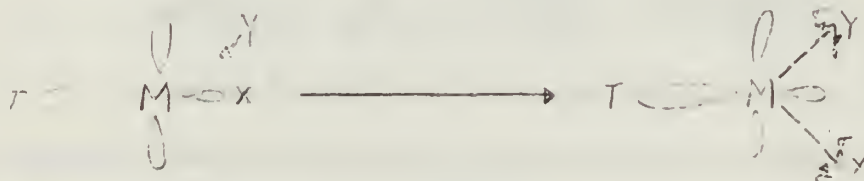


Figure 2-2: Change in metal p orbitals structure in square-planar substitution.

Second, the " π -bonding" theory attributes the trans effect to the ligands ability to form d-d π bonds with the metal atom. This is shown in Figure 2-3, and we observe that a π -bonding ligand will withdraw electron density in the d π orbital which it shares with the ligand trans to it. This charge withdrawal makes the region around X more accessible to nucleophilic attack. A shortcoming of this theory is immediately obvious; it extends only to ligands with vacant d orbitals available to form the required π bonds. Hence, it will not apply to ligands such as NH_3 and H_2O .



Figure 2-3: π -interaction with trans ligand L, showing reduced charge density in vicinity of leaving group X.

CIS EFFECT

In contrast to the profound influence of groups trans to the leaving group, the cis ligands have only a small effect. The cis effect may be defined as the effect of a coordinated group upon the rate of substitution reactions of ligands adjacent to it in a metal complex. Poë³ and Vaughn³ discuss the accelerative properties of a cis NH_3 , while Martin⁷ defines the cis effect due to Cl^- as a retarding effect. The cis effect, in general, will be defined here as a retarding effect.

Although the differences in cis effects are small, in some cases they can be more important than trans effects, particularly when comparing groups of weak and nearly equal trans effect. Martin, et al., in studies of the rates of aquation of the chloro-amine Pt (II) complexes, found that the difference in cis effects of NH_3 and Cl^- ($\text{Cl}^- > \text{NH}_3$) was larger than their trans effect difference ($\text{Cl}^- > \text{NH}_3$). The cis ligands, therefore, determine the relative rates in these complexes.

⁷⁾ M. A. Tucker, C. B. Colvin, and D. S. Martin, Inorg. Chem., 3, 1373 (1964)

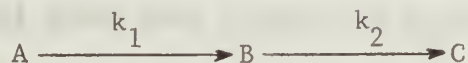
SECTION III

MATHEMATICAL MODELS OF KINETICS

The study of reaction kinetics requires the measurement of some changing aspect of the system as a function of time. Among the methods usable for these measurements are spectrophotometry, potentiometry, chromatography, coulometry, and polarimetry. Of these, ultraviolet-visible spectrophotometry was selected as the method most likely to give valid, reproducible results with a minimum of time and labor.

The instrument to be used, (a Beckmann Model DU spectrophotometer), was not capable of scanning a continuous spectrum. Therefore, a particular wavelength had to be selected at which the change in absorbance with time was proportional to the changing concentration of one of the reacting species.

To make this selection, consider the general sequence



where k_1 and k_2 are pseudo-first-order rate constants. Then the instantaneous concentrations of A and B are given by⁸

$$(3-1) \quad (A) = (A)_0 e^{-k_1 t}$$

$$(3-2) \quad (B) = \frac{k_1 (A)}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

Now, let D be the absorbance of the system, or

$$(3-3) \quad D = [\epsilon_A (A) + \epsilon_B (B) + \epsilon_C (C)] l$$

⁸⁾ A. A. Frost and R. G. Pearson, Kinetics and Mechanism, John Wiley and Sons, Inc. New York, 1953, p. 153

where ϵ_i is the molar absorptivity of the i^{th} species and l is the path length. If D_∞ is defined by

$$D_\infty = \epsilon_C (A)_0 l$$

then equation (3-3) may be rearranged to give

$$(3-4) \quad \frac{D - D_\infty}{l} = (\epsilon_A - \epsilon_C) (A) + (\epsilon_B - \epsilon_C) (B)$$

so that substitution of (A) and (B) from (3-1) and (3-2) will yield

$$(3-5) \quad \frac{D - D_\infty}{l} = [(\epsilon_A - \epsilon_C) + X (\epsilon_B - \epsilon_C)] (A)_0 e^{-k_1 t} \\ - X (\epsilon_B - \epsilon_C) (A)_0 e^{-k_2 t}$$

where $X = k_1 / (k_2 - k_1)$

Thus, either step of the sequence may be studied, providing only that the molar absorptivities are such that the unwanted term will drop out.

$\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ is known to have an absorbance maximum at 380 m μ ,³ and $\text{Pd}(\text{NH}_3)\text{Cl}_3^-$ has been reported^{2,3} to have a maximum in the vicinity of 430 m μ . Thus, it was logical to investigate the region around 405 m μ to determine the point where $\epsilon_B = \epsilon_C$.

Since, at this point, $D - D_\infty$ is a function of k_1 only, a plot of $\ln(D - D_\infty)$ versus time will be a straight line. In addition, a pseudo-isosbestic will appear as the exponential factor becomes negligible.

Using a Beckmann DB spectrophotometer, repeated scans of D vs. λ , where λ ranged from 600 — 220 m μ , were made on a reacting solution. A careful study of the resulting records indicated that, at a wavelength of 400 m μ , $\epsilon_B = \epsilon_C$. This wavelength, therefore, was used in all studies of the first step.

To find the rate constant, k_1 , from absorbance versus time measurements, it is necessary to know, or to eliminate, D_∞ . This may be done by the following stratagem. Consider a wavelength at which $\epsilon_B = \epsilon_C$. Then equation (3-5) may be written as

$$(3-6) \quad D = (\epsilon_A - \epsilon_C) l (A)_0 e^{-k_1 t} + D_\infty$$

Differentiating this with respect to time gives

$$\begin{aligned} \frac{dD}{dt} &= -k_1 (\epsilon_A - \epsilon_C) l (A)_0 e^{-k_1 t} \\ (3-7) \quad &= -k_1 (D - D_\infty) \\ &= -k_1 D + k_1 D_\infty \end{aligned}$$

So that a plot of dD/dt versus D should give a straight line with a slope of $-k_1$ and an intercept of the D axis equal to D_∞ .

To study the second step, it is necessary to find a wavelength, if one exists, where the pre-exponential factor of the first term of equation (3-5) is zero. This may occur in two regions, i.e., when $\epsilon_A > \epsilon_C > \epsilon_B$ or when $\epsilon_B > \epsilon_C > \epsilon_A$. Where these inequalities are satisfied, $D - D_\infty$ is a function of k_2 only. A plot of $\ln(D - D_\infty)$ will thus be linear with time, and a pseudo-isosbestic will occur as discussed above.

An intensive examination of the repeated scan spectra revealed neither a linear relationship between $\ln(D - D_\infty)$ and time nor an isosbestic condition except at 400 mμ. Hence, there was no wavelength where the inequalities between molar absorptivities were properly satisfied. There is, at present, no clear reason for the apparent non-existence of such a wavelength. There are, however, at least two possibilities:

- 1) The desired wavelength does not lie between 600 and 200 mμ, or

- 2) An unsuspected reaction interfered with and obscured the proper relationship.

Since this technique failed to produce the desired results, data on the kinetics of the second step had to be obtained by a different method. Recalling that the concentration of B as a function of time may be expressed as

$$(3-2) \quad (B) = \frac{k_1 (A)_o}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

if k_1 and k_2 are sufficiently different, e.g., $k_1 \gg k_2$, then, at long times,

$$(3-8) \quad (B) = -\frac{k_1 (A)_o}{k_2 - k_1} e^{-k_2 t}$$

Since $e^{-k_1 t}$ is approximately zero, the first term of (3-5) disappears, and the expression for absorbance as a function of time is just

$$(3-9) \quad D - D_\infty = -\frac{k_1}{k_2 - k_1} (\epsilon_B - \epsilon_C) (A)_o e^{-k_2 t}$$

Thus a plot of $\ln(D - D_\infty)$ versus time should give, at long times, a straight line with slope of $-k_2$ and intercept of $[k_1/(k_2 - k_1)] (\epsilon_B - \epsilon_C)(A)_o$. Figure 3-1 illustrates this condition.

In this case, k_1 may be determined by subtracting the actual values of $D - D_\infty$ from those obtained by extrapolating the k_2 line to corresponding times to give a difference, Δ . A plot of the natural logarithm of Δ versus time should be linear with slope of $-k_1$ and intercept of $(\epsilon_B - \epsilon_A)[A]_o$. Figure 3-2 gives an illustration of this procedure.

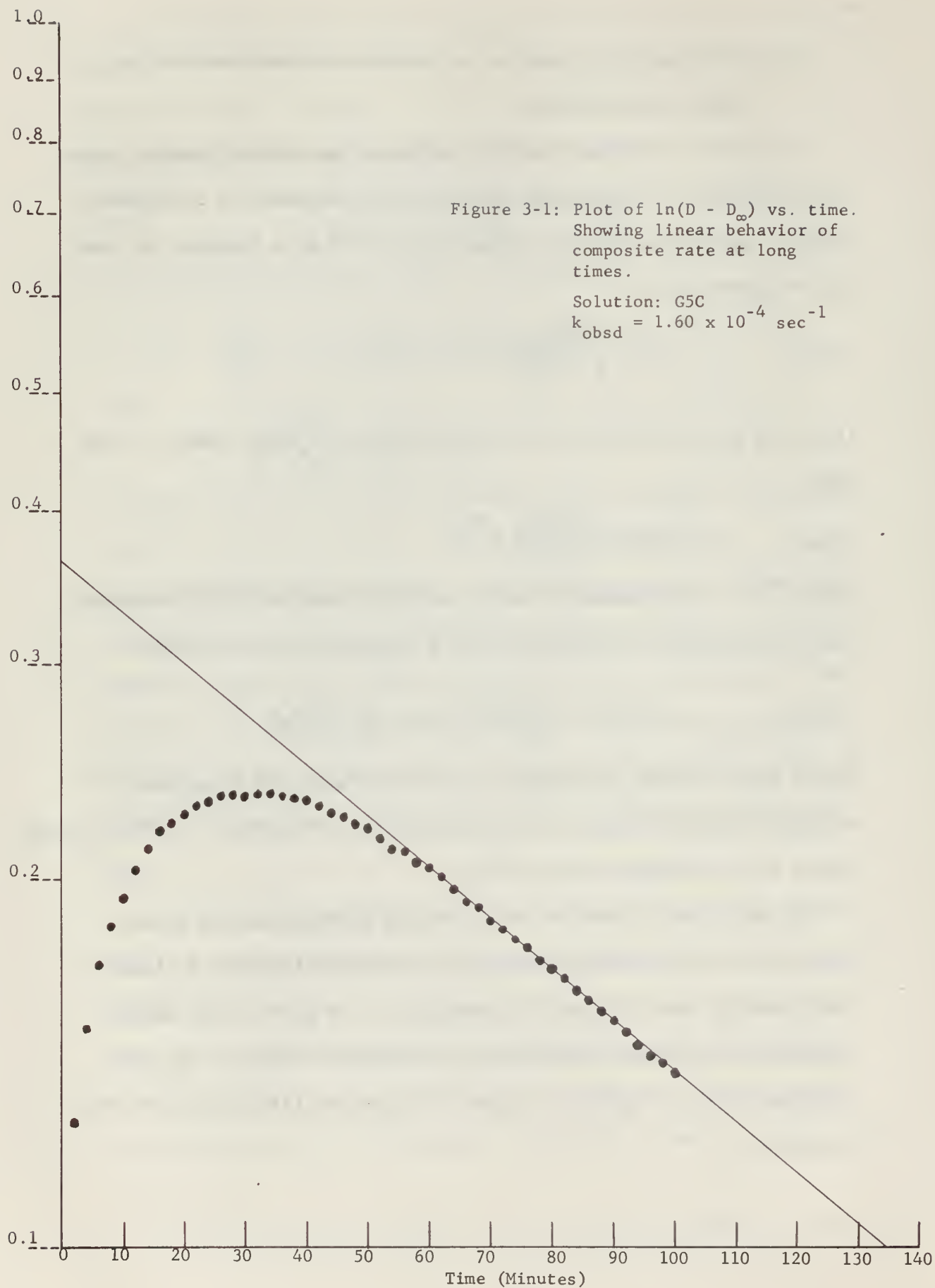


Figure 3-2: Plot of $\ln \Delta$ versus time.
 Showing linear behavior of
 the difference between a
 composite rate and one of
 its component rates.

Solution: G5C
 $k_{\text{obsd}} = 1.05 \times 10^{-3} \text{ sec}^{-1}$

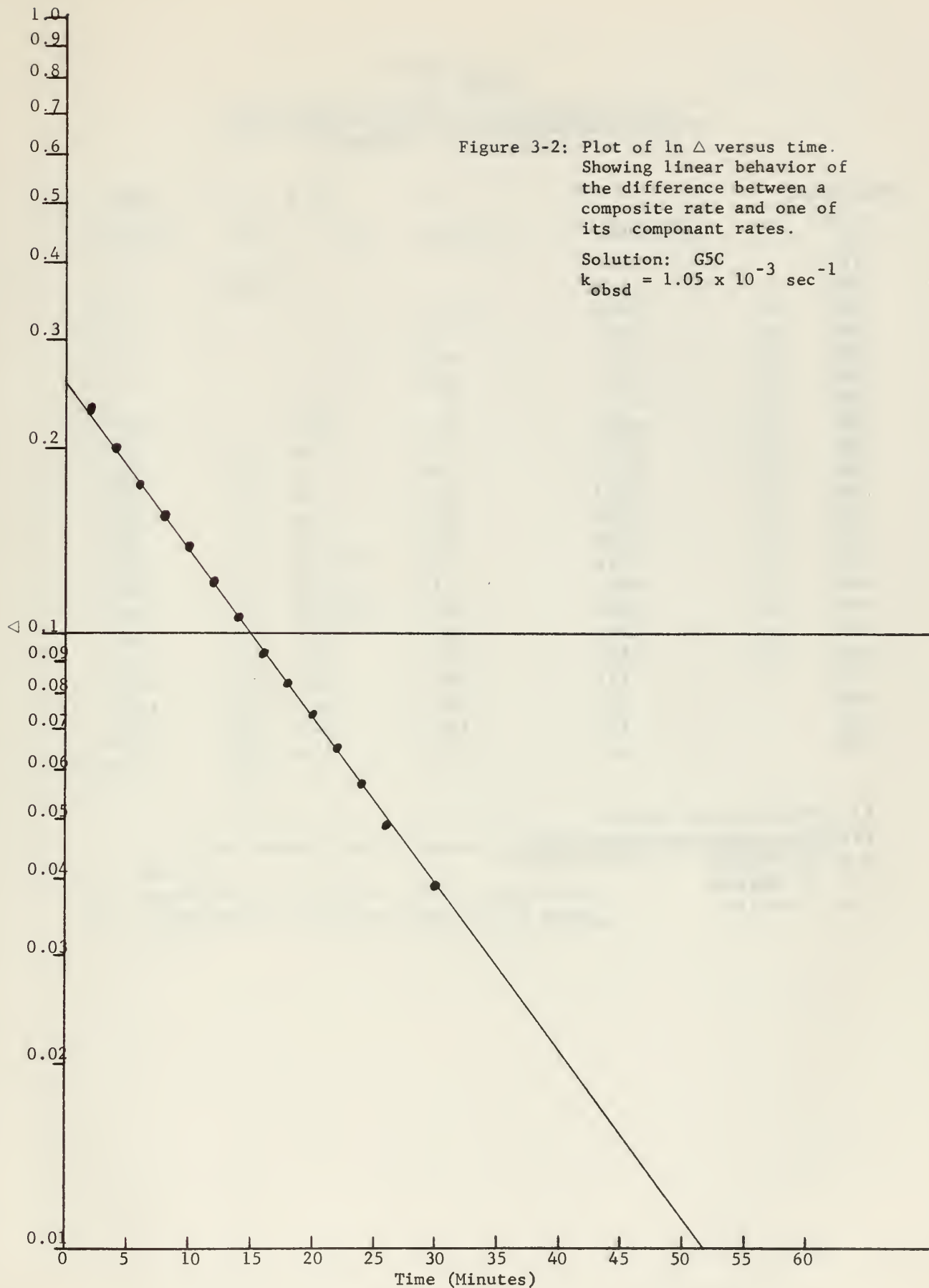


TABLE 3-1

MOLAR ABSORPTIVITIES OF $\text{PdCl}_4^{=}$ IN 3M HCl

Wavelength (m μ)	C-6	C-7	C-8	Mean
310	1337			
320	720			
330	555			
340	441			
345		362		
350	267	285		
355			197	
360	117	137	135	136
370	39	57	58	57
380	17	29	29	29
390	21	27	27	27
400	36	38	38	38
410	56	55	53	54
420	76	72	72	72
430	101	93	93	93
440	122	115	113	114
450	146	135	134	134
460	166	155	151	153
470	181	165	163	164
480	177	164	163	164
490	162	152	145	149
500	137	127	124	126

All solutions are 3M HCl.

Palladium concentrations were:

C-6 0.000125M

C-7 0.000471M

C-8 0.00131M

TABLE 3-2
MOLAR ABSORPTIVITIES OF THE CHLOROAMMINE
COMPLEXES OF PALLADIUM

Wavelength (mμ)	Pd4	Pd3	<u>cis</u> -Pd2	<u>trans</u> -Pd2 ^e	Pd1 ^e	Pd0 ^e
280	11200 ^a					148
290			1500 ^b	15	80	194
300				35	100	197
310				45	160	161
320				77	211	105
330				88	233	61
340				102	228	36
350				114	187	24
360	136			135	130	17
370	57			159	74	13
380	29			159	44	9
390	27			150	31	
400	38	127 ^c		127	19	
410	54			95	16	
420	72	130 ^d		59	16	
430	93			33	14	
440	114			19	14	
450	135					
460	153					
470	164					
480	164					
490	149					
500	126					

a) S. C. Srivastava and L. Newman, Inorg. Chem., 5, 1506 (1966)

b) Ref. 3

c) Approximate value from first step studies

d) Approximate value from second step studies

e) Ref. 9

In order to follow the change in absorbance due to B with minimum interference, it was desirable to choose a wavelength where $\epsilon_A \approx \epsilon_C$. Previous work by Reinhardt⁹ had produced values of trans-Pd2 molar absorptivities in the range 290 - 440 m μ . Little information was available, however, on either cis-Pd2 or Pd4. It seemed reasonable to assume that the molar absorptivities of the cis isomer of Pd2 would not vary greatly from those of the trans isomer³, therefore the available information was used without correction.

Determination of values for Pd4 was carried out using 1 cm. cells in the Beckman DU at room temperature. Three solutions of $(\text{NH}_3)_2\text{PdCl}_4$ were made up in ca. 3M HCl and run against a reference solution of 3M HCl. Values obtained are displayed in Table 3-1. Palladium concentration in these solutions was determined gravimetrically as the salt of dimethylglyoxime¹⁰.

Table 3-2 is a compilation of available molar absorptivities for the entire chloroammine series of palladium. Inspection of the data for trans-Pd2 and Pd4 indicates the $\epsilon_A \approx \epsilon_C$ at about 418 m μ , consequently this wavelength was selected for study of the second step.

⁹) R. A. Reinhardt, Naval Postgraduate School, private communication, 1967

¹⁰) F. P. Treadwell and W. T. Hall, Analytical Chemistry, Vol. II John Wiley and Sons, Inc., New York, 1942, p. 140

SECTION IV

EXPERIMENTAL METHODS

MATERIALS HANDLING

Ammonia was derived from the dissociation of ammonium ion, according to the relationship

$$(4-1) \quad (\text{NH}_3) = K_{\text{NH}_3} \frac{(\text{NH}_4^+)}{(\text{H}^+)}$$

Since the anticipated form of the rate law required knowledge of the ammonia concentration, the pH of the system had to be controlled by addition of a buffering solution. The acetic acid-acetate ion system was chosen for two reasons:

- 1) It gave the desired pH
- 2) It was shown not to interfere with the reactions being studied¹¹.

The hydrogen ion concentration in acetic is given by

$$(4-2) \quad (\text{H}^+) = K_{\text{HOAc}} \frac{(\text{HOAc})}{(\text{OAc}^-)}$$

Substitution of this into (4-1) gives

$$(4-3) \quad (\text{NH}_3) = \frac{K_{\text{NH}_4} + (\text{OAc}^-)}{K_{\text{HOAc}} (\text{HOAc})} (\text{NH}_4^+)$$

so that the ammonia concentration will be a constant multiple of the ammonium ion concentration.

The acetic acid was made up by diluting glacial acetic acid to approximately 0.1 M, then standardizing against freshly prepared NaOH which had, in turn, been standardized with potassium acid phthalate.

¹¹ N. Layton, D. W. Sink, and J. R. Durig, J. Inorg. Nuclear Chem., 28, 1965 (1966)

Acetate ion was provided in the form of anhydrous NaOAc. This was oven-dried at 110°C and stored in a glass desiccator until used.

The buffer solution was made up by adding a calculated amount of dry NaOAc to a known volume of acid. Concentrations were calculated so that 10 ml of buffer solution in 100 ml of reacting solution gave a acid concentration of 0.01 M.

Palladium was supplied as dry Na_2PdCl_4 . Palladium stock solutions were made up in 100 ml portions as required and kept in a constant temperature bath at the temperature currently being used for kinetic runs. Stock solutions were ca. 0.005 M Pd in a 1 M NaCl solution, the Cl^- serving to repress hydrolysis and maintain the Pd in the $\text{PdCl}_4^{=}$ complexed state.

Two sources of NH_4^+ were used, depending on the chloride ion concentration desired. All 1 M Cl^- solutions used NH_4Cl , while all other solutions were made up from NH_4ClO_4 . Preparation varied slightly in that the NH_4Cl was used as a dry solid, while the perchlorate was made up in a 1 M solution and pipetted into the reacting solution.

Chloride was added as dry NaCl with NaClO_4 used where necessary to maintain the desired ionic strength. In both cases, the salts were oven dried at 110°C and stored in a glass desiccator until used.

EXPERIMENTAL PROCEDURES

For each run, the predetermined amounts of dry reagents (NaCl , NaClO_4 , and NH_4Cl) were weighed and transferred quantitatively to a clean, dry 125 ml erlenmeyer flask. Ten milliliters of buffer solution and the desired quantity of NH_4ClO_4 stock solution were pipetted into the flask. The solution was stirred magnetically to dissolve the dry constituents and made up to a previously calibrated 90 ml mark. The

flask was placed in a constant temperature bath for a minimum of three hours before a kinetic run was commenced.

Palladium stock solution was made up in a similar manner, except that the NaCl was fully dissolved prior to adding the solid Na_2PdCl_4 .

All kinetics runs were made using a Beckmann DU spectrophotometer equipped with a Beckmann thermospacer on each end of the cell compartment and a thermojacket surrounding the cells. The thermojacket assembly consisted of a base plate which replaced the Beckmann 10 cm cell holder and was located by the same notched adjusting rod used with the Beckmann holder.

The jacket was fabricated from rectangular brass waveguide. Brass tubing was silver soldered inside the waveguide, then bored to finished diameter to accept the cells used. Small (1/8 in. O.D.) brass tubes in diagonally opposite corners provided coolant inlet and exit passages.

A new cell compartment cover was made to provide interior and exterior attachments for Tygon tubing which carried the coolant. A reducer in the cover accepted the 1/4 in. I.D. tubing used externally and the 1/8 in. I.D. tubing used for final connections to the thermojacket.

Water from a constant temperature bath was circulated through both thermospacers and the thermojacket by a submerged pump operating in suction. Initial connection from the bath was through an insulated stainless steel tube.

In addition to the DU, a Beckmann DB recording spectrophotometer without temperature control was employed for rough qualitative analysis of the Pd stock solutions and all run solutions.

Cells used were, for the DU, 10 cm cylindrical Beckmann standard silica cells. For work on the DB, 1 cm square Beckmann standard silica cuvettes were utilized.

At least one hour prior to any run, the DU and thermostated circulating pump were turned on and allowed to warm up. The DB was warmed up approximately 20 minutes before use, although this was not considered critical.

Prior to each run, the sample cell was rinsed five times with distilled water and three times with 95% ethanol. It was then oven-dried, aspirated with house vacuum, stoppered, and placed in the thermostated. The reference cell was rinsed five times with distilled water and three times with reference solution. It was then filled with solution and placed in the thermostated to equilibrate at least 30 minutes prior to starting a run. Reference solution for all runs was identical to the run solution save only for the omission of palladium.

About 20 minutes prior to commencing a run, a sample of Pd stock solution was scanned from 600-340 m μ in the DB to ensure that no hydrolysis had occurred. The DB was left on (but not recording) at 470 m μ during the kinetic run to further monitor the stock solution. Since the absorbance of Pd(OH)₂ is quite different at 470 m μ than that of PdCl₄⁼, the onset of hydrolysis is easily seen by a large change in absorbance.

Just before starting a run, the DU was nulled using the reference solution. To actually start a run, the required amount (usually 10 ml) of Pd stock solution was pipetted into the flask containing the run solution using a delivery pipet and bulb. The clock was started when half the solution had been delivered. The flask was removed from the

bath, swirled vigorously to mix the solution, and about half the solution was poured into a clean, dry 50 ml beaker and then into the cell. The thermojacket and cells were placed in the instrument. The null was checked, and readings were begun. Using this procedure, the first reading could be taken about 90 seconds after mixing.

For first step studies, readings were taken at intervals of 2.5 or 5 minutes, depending on the speed of reaction. In either case, the instrument null was checked just prior to each reading. Readings were continued until the change in absorbance was less than 0.005 or until 20 points had been recorded.

For second step studies, readings were taken at 2.5 minute intervals for 100 minutes.

Upon completion of each run, a sample of run solution was withdrawn from the cell and scanned over a range 600-200 $m\mu$ in the DB to determine the approximate composition by observing the wavelengths at which maxima occurred. Comparison with known complex maxima thus gave a rough qualitative complex composition.

It was planned to use atomic absorption spectrometry to determine the Pd concentration in the unused portion of the run solutions. Accordingly, four run solutions were made up in sufficient quantity (500 ml) to enable determination of Pd gravimetrically¹⁰. These solutions were used to establish a reference curve on the Perkin Elmer Model 303 spectrophotometer and all other run solutions were determined from this. Figure 4-1 illustrates the reference curve and Table 4-1 lists all run solutions and their compositions.

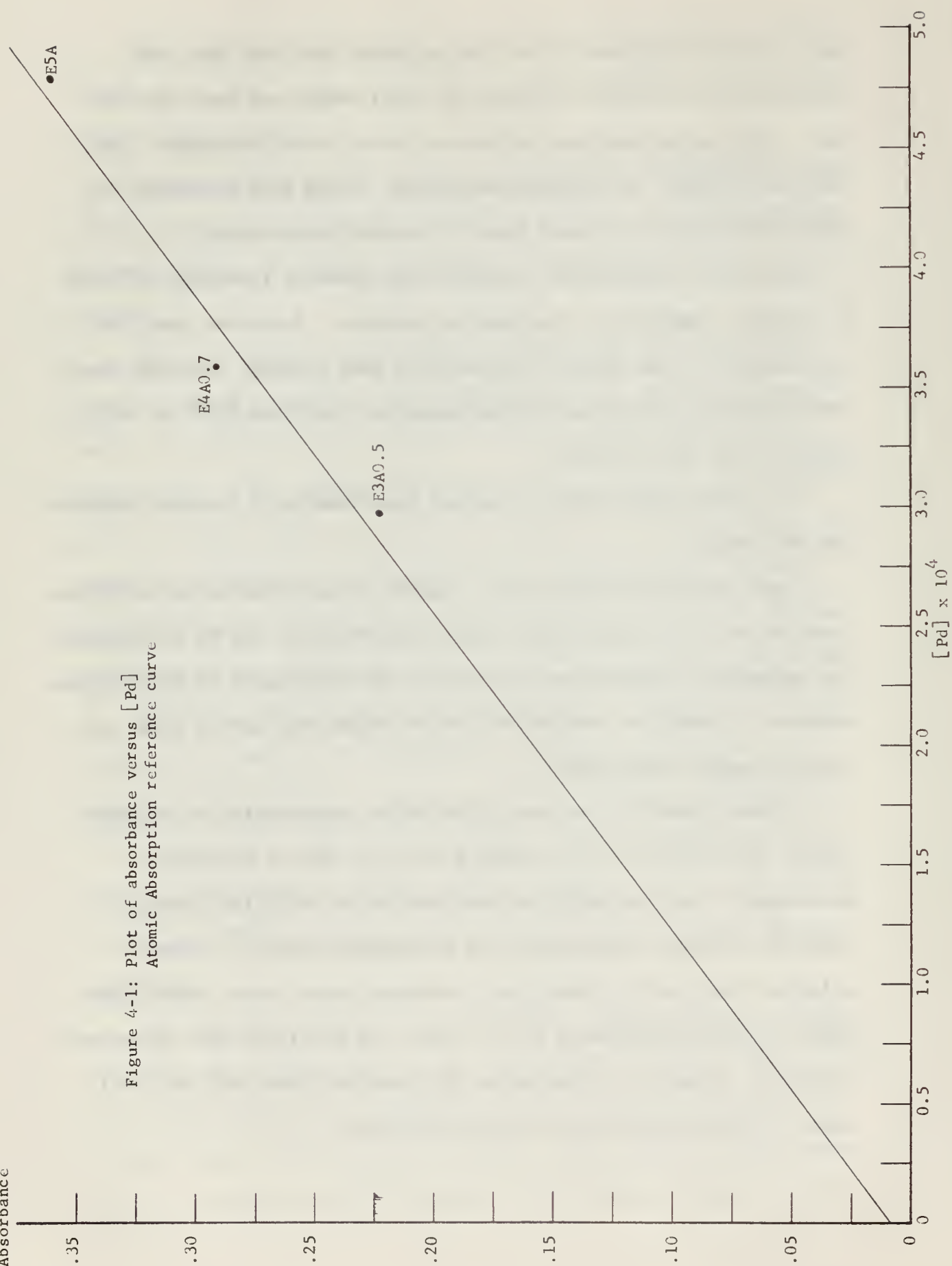


TABLE 4-1

Solution	10^4 [Pd]	Solution	10^4 [Pd]
D4A	3.05	D5D0.5	4.51
D5A	2.16	D4E	2.55
D4B	3.21	D5F	4.41
D4B0.7	3.22	E5A	4.81
D4B0.5	3.43	E4A0.7	3.60
D5B	2.04	E3A0.5	2.98
D4B(2Ac)	3.27	E5B	4.42
D4B($\frac{1}{2}$ Ac)	3.02	E5B0.7	4.47
D4C	3.30	E5B0.5	4.55
D5C	2.00	E5C	4.07
D5C0.7	4.14	E5C0.7	4.55
D5C0.5	4.42	E5C0.5	4.54
D4D(I)	3.28	G5C	3.85
D4D(II)	3.25	G5C0.75	4.05
D5D0.7	4.45	G5A0.5	4.36

SECTION V

DATA HANDLING AND RESULTS

METHODS

As previously described, observed pseudo-first-order rate constants for the first step were obtained by plotting dD/dt as a function of D and measuring the slope of the resulting straight line. Absorbance data from all runs is listed in Appendix A.

The computer program listed in Appendix B was written to evaluate dD/dt (using the approximation $dD/dt \approx \Delta D/\Delta t$), plot the results, and fit the best straight line to the points. Figure 5-1 is a sample of this plot. A linear least-squares fit was used, and standard deviations were computed for both the slope and intercept.

On the basis of previous results^{3,11}, it was assumed that the reactions:

- 1) Were first-order in complex,
- 2) Were independent of pH, and
- 3) Did not exhibit any acetate ion effects.

To verify the first assumption, data runs were made at varying values of Pd concentrations. Computer reduction of the data yielded k_{obsd} values which were identical within experimental error. These results are displayed in Table 5-1.

TABLE 5-1

Run	10^4 (Pd)	$10^4 k_{\text{obsd}}$
D4A	3.05	2.59
D5A	2.16	2.59
D4B	3.21	5.78
D5B	2.04	5.64
D4C	3.30	1.34
D5C	2.00	1.40

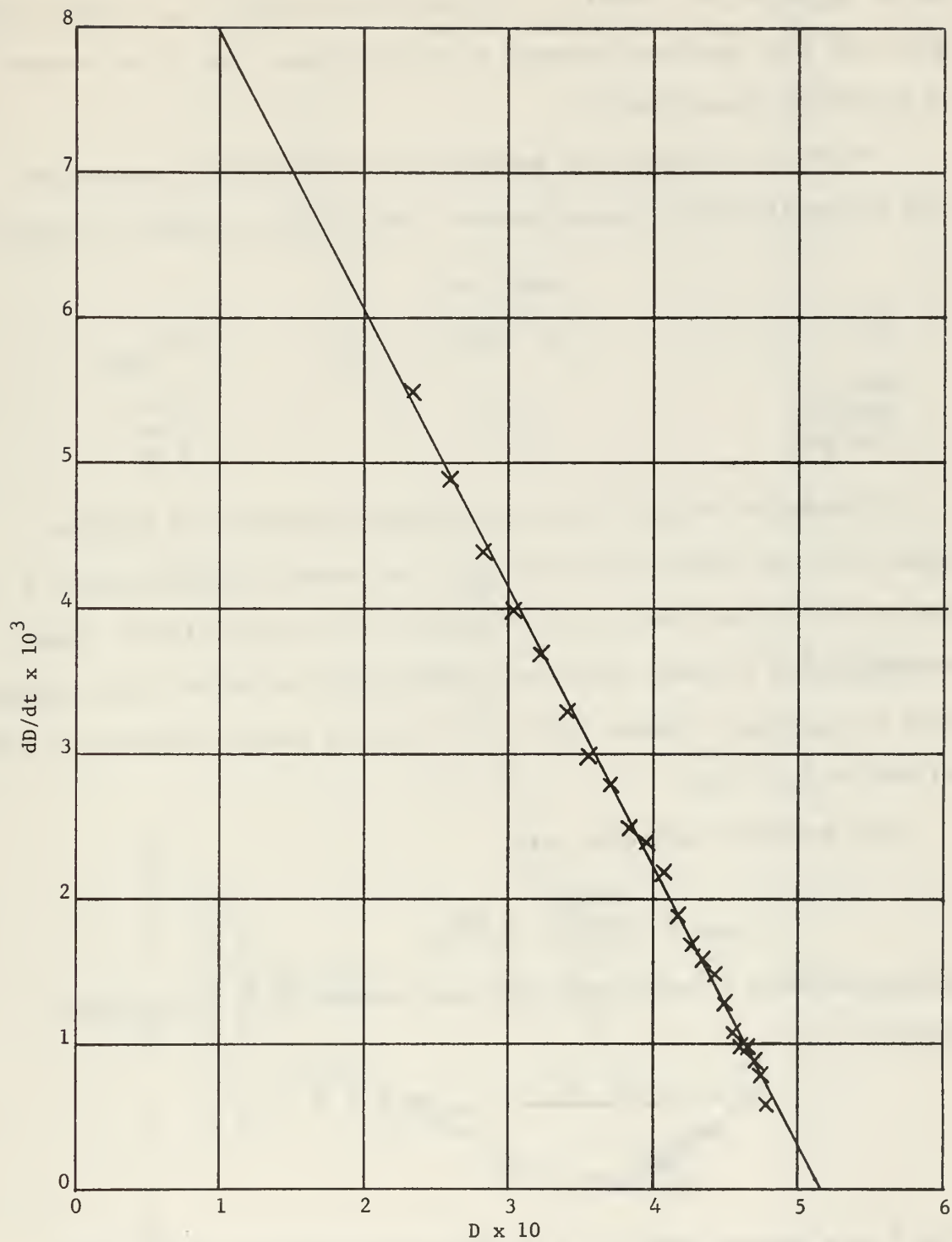


Figure 5-1: Program KINET plot of dD/dt versus D for solution E4A0.7
 $k_{\text{obsd}} = 3.19 \times 10^{-4} \text{ sec}^{-1}$; $D_{\infty} = 0.517$

To verify pH dependence, a data run was made at a changed buffer ratio, giving a pH of about 4. The resulting value of k_{obsd} agreed quite well with that predicted assuming no pH dependence. The value observed is plotted on Figure 5-2.

Proof of no acetate ion interference was obtained by making two runs at varying buffer concentrations. The results are shown in Table 5-2.

TABLE 5-2

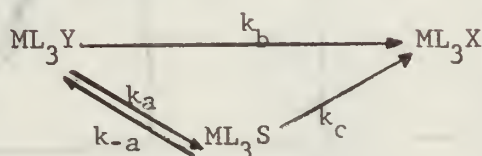
Run	10^2 (HOAc)	$10^4 k_{\text{obsd}}$
D4B	1.0	5.78
D4B(2Ac)	2.0	5.42
D4B($\frac{1}{2}$ Ac)	0.5	5.04

To determine values for the actual rate constants, the observed values from the computer were divided by the ammonia concentration. A plot of these values versus the reciprocal of the free chloride concentration yielded a linear relationship from which the actual rate constants could be obtained. Figures 5-2 and 5-3 show the results obtained at 25°C and 30°C respectively.

This procedure indicates that:

$$k_{\text{obsd}} = k_1 \frac{(\text{NH}_3)}{(\text{Cl}^-)} + k_2 (\text{NH}_3)$$

A mechanism which is consistent with this indication is the dual-path mechanism



where S is a solvent molecule, X is the entering group, and Y is the leaving group. Now, if $k_{-a}(Y) \gg k_c(X)$, the rate law may be shown to be:

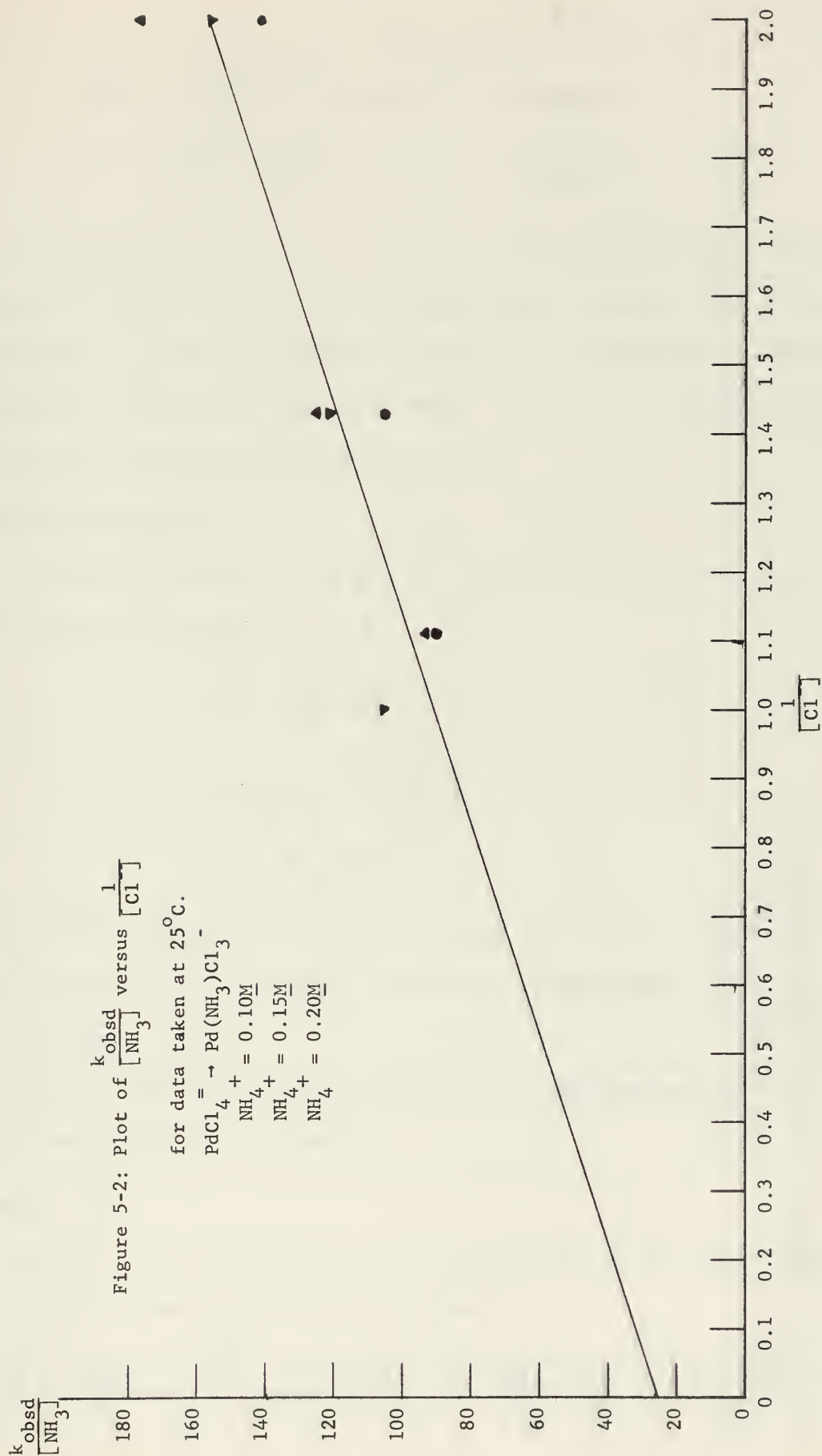


Figure 5-3: Plot of $\frac{k_{\text{obsd}}}{[\text{NH}_3]}$ versus $\frac{1}{[\text{Cl}^-]}$

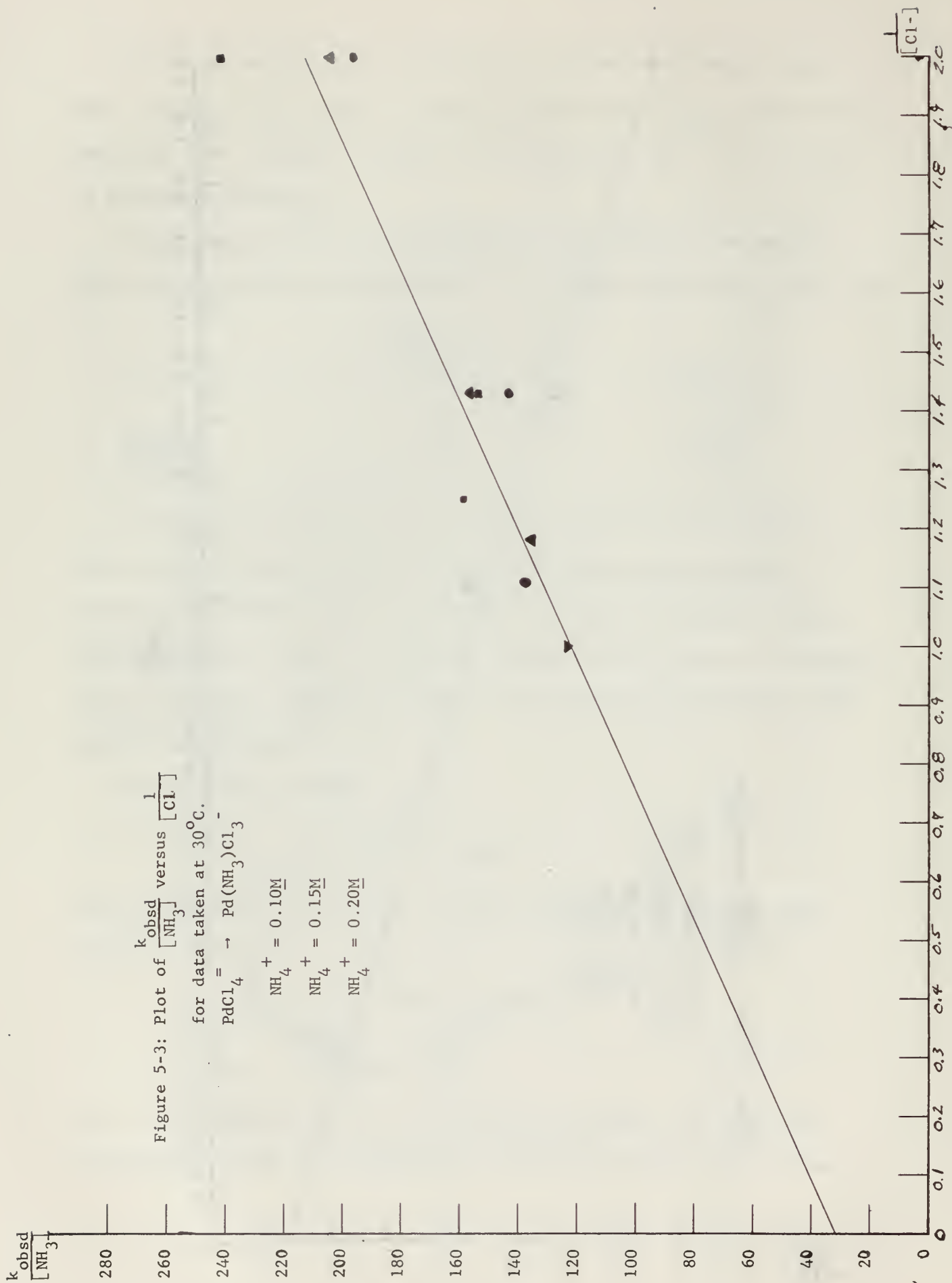
for data taken at 30°C.



$$\text{NH}_4^+ = 0.10\text{M}$$

$$\text{NH}_4^+ = 0.15\text{M}$$

$$\text{NH}_4^+ = 0.20\text{M}$$



$$\begin{aligned} \text{Rate} &= \left\{ \frac{k_a k_c (X)}{k_{-a} (Y)} + k_b (X) \right\} & (\text{Complex}) \\ &= \left\{ k_1 \frac{(X)}{(Y)} + k_2 (X) \right\} & (\text{Complex}) \end{aligned}$$

For the second step i.e., $\text{Pd}(\text{NH}_3)\text{Cl}_3^- \longrightarrow \text{Pd}(\text{NH}_3)_2\text{Cl}_2$, observed values of the pseudo-first-order constants were extracted from a plot of $\ln(D - D_\infty)$ versus time as discussed previously. The values obtained were treated as described for the first step. Figure 5-4 illustrates the relationship obtained for the second step.

ACTIVATION PARAMETERS

Activation parameters for the first step were calculated using the following relationships:

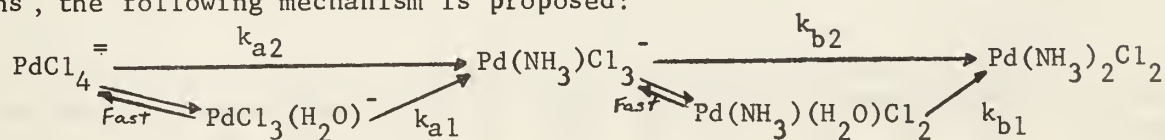
$$\begin{aligned} \Delta F^* &= RT \ln \left[\frac{k_B T}{h k_r} \right] \\ \Delta H^* &= R \left[T \frac{d(\ln k_r)}{d\left(\frac{1}{T}\right)} \right] \\ \Delta S^* &= \frac{\Delta H^* - \Delta F^*}{T} \end{aligned}$$

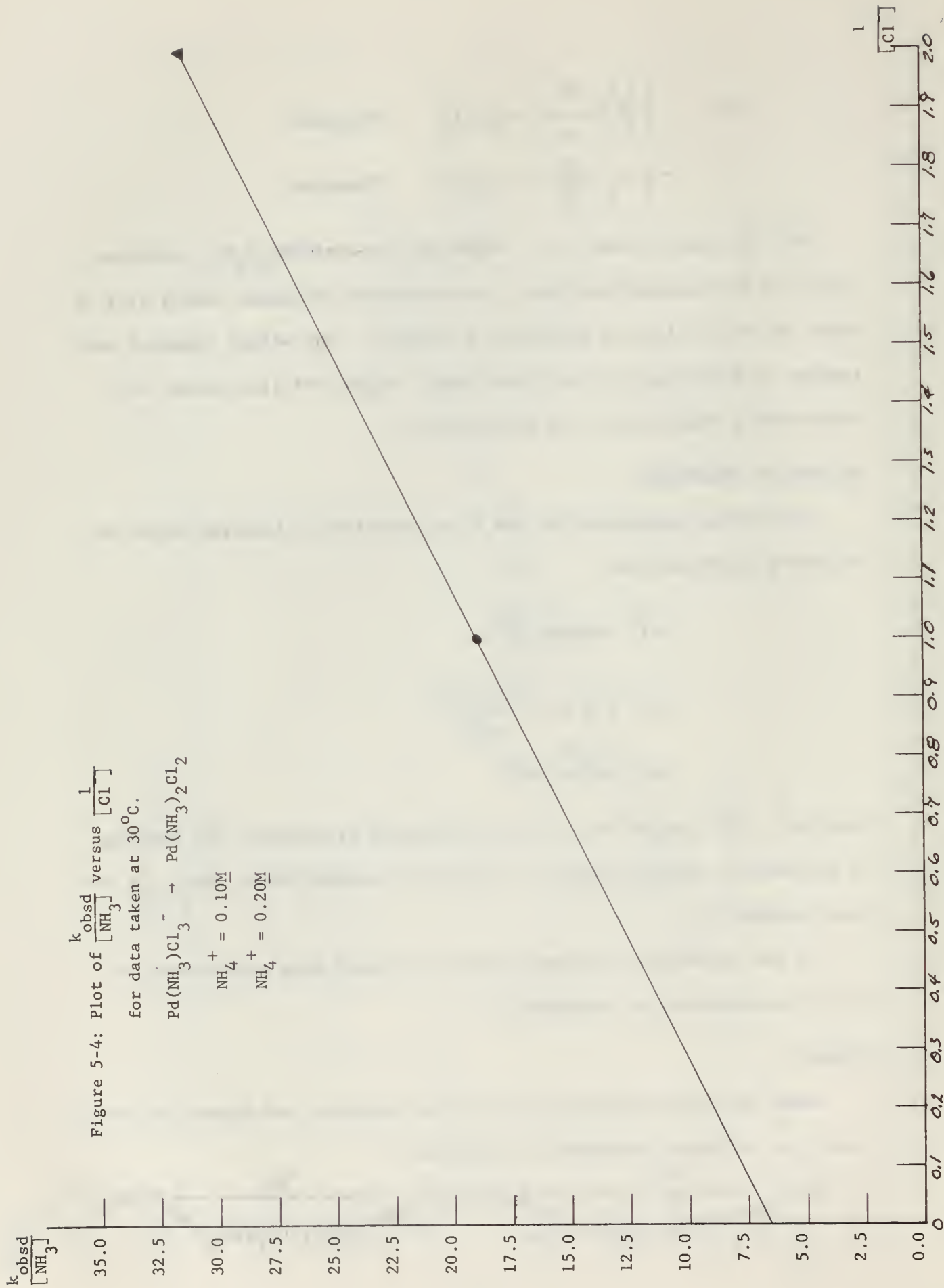
where ΔF^* , ΔH^* , and ΔS^* are the free energy of activation, the enthalpy of activation, and the entropy of activation respectively, and k_r is the rate constant.

It was impossible to characterize the second step sufficiently to permit determination of parameters.

SUMMARY

Based on the relationship of the rate constants and ligand concentrations, the following mechanism is proposed:





Based on the results of the aforementioned plots, the following values of rate constants and activation parameters are also proposed:

	25° C	30° C	ΔH^* kcal/mole	ΔS^* e.u.
k_{a1}	65.4 sec ⁻¹	89.8 sec ⁻¹	12.0	-10.0
k_{a2}	25.2 M ⁻¹ sec ⁻¹	31.3 M ⁻¹ sec ⁻¹	8.4	-24.0
k_{b1}		12.5 sec ⁻¹		
k_{b2}		6.5 M ⁻¹ sec ⁻¹		

SECTION VI

DISCUSSION

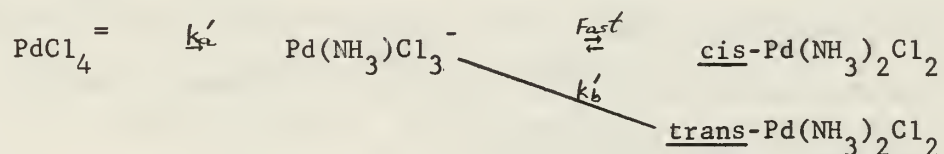
As noted in the previous section, the rate of NH_3 substitution into $\text{Pd}(\text{NH}_3)\text{Cl}_3^-$ is considerably slower than the rate of substitution into $\text{PdCl}_4^{=}$. This is contrary to the expected situation, since, if cis Pd2 is formed, the trans effect of Cl^- should enhance the rate of substitution. Furthermore, Durig, et. al.,¹¹ prepared the cis isomer in essentially the same manner as used here so that any explanation must account for both the formation of cis-Pd2 and the decrease in rate of the second step.

Equilibrium constants were calculated using Poë's data³ for the reverse reaction and information determined in this study for the forward reaction. Assuming that the rate constants reported in Section V are for the formation of cis-Pd2 only, the resulting ratio of cis-Pd2 to Pd3 is only about 0.034. If, however, the rates are assumed to be for the formation of trans-Pd2, the ratio of trans-Pd2 to Pd3 is about 5. Thus if the cis isomer alone is formed, the equilibrium condition must be reached rather quickly. Further, there can not be a large amount of Pd2 formed. While no information is available on the kinetics of cis formation, spectrophotometric scans of reacted solutions indicated the presence of far to much Pd2 to be compatible with this hypothesis. It is probable, therefore, that the solution contained an appreciable concentration of the trans isomer at the time the scans were made.

Quantitative information on the rate of cis-trans isomerization is not presently available, but qualitative data reported by Durig, et. al.¹¹, indicates that the rate of isomerization is probably so slow as to be

negligible under these conditions. Therefore, if the trans isomer is present, it must have been a product of the reaction of Pd3 and ammonia.

In view of the foregoing information, the following reaction pathway is proposed:



therefore, the second step rate constants given in the last section are thought to be those for the formation of the trans isomer.

This conclusion is supported by the large trans yield obtained by Durig, et. al.¹¹, in their attempts to reproduce Grinberg's¹² results in synthesis of the cis isomer. It is also supported by their synthesis procedure of the cis isomer, since the rapid formation of the cis isomer will allow precipitation of it in a relatively pure form.

Assuming no charge effect on the rates, the rate of trans-Pd2 formation (including a statistical correction), is $\frac{4k_{B2}}{k_{A2}} = 0.83$. Due to incomplete characterization of the second step, however, it is not possible to ascribe this deviation to any particular effect. If the cis effect is operative in this system, it must be small in contrast to the very large cis effect previously reported^{2,3} for reverse reactions in the series.

The kinetics of the formation of cis-Pd2 are not known. There were, however, experimental indications of a very fast step which may be attributable to this reaction. From these indications, the rate of cis formation, including a statistical correction, may be estimated to be ca. 14 times as fast as the rate of formation of Pd3. This value is comparable to previously reported² trans effect accelerations in the chloroammine Pd(II)

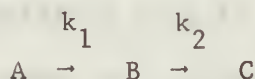
system. In view of this information, therefore, it is proposed that the trans effect is operative in this system. The very rapid formation of cis-Pd2 indicates that the Cl^- ligands exert a definite labilizing effect on the ligand trans to them in the complexes.

The equilibrium constants for the first step, i.e., $\text{Pd4} \rightarrow \text{Pd3}$, was calculated using kinetic data reported by Poë¹³ for the reverse reaction and data generated in this study for the forward direction. For the Cl^- independent path, at 25°C.

$$K_{\text{eq}} = \frac{k_{\text{fwd}}}{k_{\text{rev}}} = 14.8 \times 10^6$$

so that, at the equilibrium point, the ratio of Pd3 to Pd4 is at least 45 under the conditions used here.

According to Frost and Pearson¹³, the maximum concentration of the intermediate B, in the general series reaction



is given by the relation:

$$\frac{[\text{B}]}{[\text{A}]_0} = \kappa / (1 - \kappa)$$

where $\kappa = k_2/k_1$.

Using this equation with $k_1 = 25.2$ and $k_2 = 5.2$, the maximum concentration of B, i.e., Pd3, may be shown to be:

$$\frac{[\text{B}]}{[\text{A}]_0} = 0.664 = \frac{[\text{Pd3}]}{[\text{Pd4}]}$$

Thus, it is evident that the equilibrium condition is not reached in the first step.

¹³) A. A. Frost and R. G. Pearson, Kinetics and Mechanism, John Wiley and Sons, Inc., New York, 1953, p. 155

BIBLIOGRAPHY

1. Reinhardt, R. A., N. L. Brenner, and R. K. Sparkes, Inorg. Chem., 6, 254 (1967).
2. Reinhardt, R. A., and R. K. Sparkes, ibid, 6, 2190 (1967).
3. Poë, A. J. and D. H. Vaughn, Inorg. Chem. Acta., 1, 255 (1967).
4. Basolo, F. and R. G. Pearson, Mechanisms of Inorganic Reactions, John Wiley and Sons, Inc., New York, 1967, pp. 377-378
5. Basolo, F. and R. G. Pearson, ibid, p. 356.
6. Langford, C. H. and H. B. Gray, Ligand Substitution Processes, W. A. Benjamin, Inc., New York, 1966, pp. 25-29
7. Tucker, M. A., C. B. Colvin, and D. S. Martin, Inorg. Chem., 3, 1373 (1964).
8. Frost, A. A. and R. G. Pearson, Kinetics and Mechanism, John Wiley and Sons, Inc., New York, 1953, p. 153
9. Reinhardt, R. A., Naval Postgraduate School, private communication, 1967.
10. Treadwell, F. P. and W. T. Hall, Analytical Chemistry, Vol. II, John Wiley and Sons, Inc., New York, 1942, p. 140
11. Layton, R., D. W. Sink, and J. R. Durig, J. Inorg. Nuclear Chem., 28, 1965 (1966).
12. Grinberg, A. A. and V. M. Shulman, Dokl. Akad. Nauk SSSR, 215 (1933).
13. Frost, A. A. and R. G. Pearson, Kinetics and Mechanism, John Wiley and Sons, Inc., New York, 1953, p. 155

APPENDIX A

Absorbance data from all runs used in calculation of first and second step rate constants.

Index of run identifiers:

1st character - Primary series designator

D - 1st step, 30°C data

E - 1st step, 25°C data

G - 2nd step, 30°C data

2nd character - Relative Pd concentration within a primary series

3rd character - Relative NH_4^+ concentration within a primary series

Supplimentary information where required is annotated following the identifier.

Solution D4A

(Pd) = 0.000305 M ; (Cl⁻) = 0.95 M ; (NH₄⁺) = 0.05 M

Time (Sec)	Absorbance	Time (Sec)	Absorbance
1620	0.290	6000	0.461
1800	0.301	6300	0.466
2100	0.319	6600	0.472
2400	0.336	6900	0.478
2700	0.352	7200	0.483
3000	0.364	7500	0.488
3300	0.378	7800	0.491
3600	0.391	8100	0.496
3900	0.403	8400	
4200	0.414	8700	0.502
4500	0.424	9000	0.504
4800	0.432	9300	0.507
5100	0.440	9600	0.511
5400	0.447	9900	0.512
5700	0.455		

Solution D5A

(Pd) = 0.000216 M ; (Cl⁻) = 0.95 M ; (NH₄⁺) = 0.05 M

Time (Sec)	Absorbance	Time (Sec)	Absorbance
1800	0.190	5400	0.286
2100	0.202	5700	0.290
2400	0.213	6000	0.294
2700		6300	0.298
3000	0.231	6600	0.302
3300	0.240	6900	0.305
3600	0.248	7200	0.308
3900	0.255	7500	0.311
4200	0.263	7800	0.314
4500	0.269	8100	0.316
4800	0.275	8400	0.318
5100	0.280		

Solution D4B

(Pd) = 0.000321 M ; (Cl⁻) = 0.90 M ; (NH₄⁺) = 0.10 M

Time (Sec)	Absorbance	Time (Sec)	Absorbance
1260	0.332	3960	0.475
1560	0.361	4260	0.482
1860	0.384	4560	0.487
2160	0.405	4860	0.491
2460	0.442	5160	0.493
2760	0.436	5460	0.497
3060	0.448	5760	0.499
3360	0.460	6060	0.500
3660	0.468		

Solution D4B0.7

(Pd) = 0.000322 M ; (Cl⁻) = 0.70 M ; (NH₄⁺) = 0.10 M

Time	Absorbance	Time	Absorbance
300	0.226	3300	0.458
600	0.270	3600	0.464
900	0.306	3900	0.469
1200	0.339	4200	0.473
1500	0.365	4500	0.479
1800	0.387	4800	0.480
2100	0.407	5100	0.482
2400	0.424	5400	0.484
2700	0.435	5700	0.486
3000	0.447	6000	0.488

Solution D4B0.5

(Pd) = 0.000343 M ; (Cl⁻) = 0.50 M ; (NH₄) = 0.10 M

Time	Absorbance	Time	Absorbance
300	0.266	2400	0.469
600	0.318	2700	0.480
900	0.359	3000	0.488
1200	0.394	3300	0.493
1500	0.421	3600	0.497
1800	0.441	3900	0.498
2100	0.457	4200	0.499

Solution D5B

(Pd) = 0.000204 M ; (Cl) = 0.90 M ; (NH₄) = 0.10 M

Time	Absorbance	Time	Absorbance
1200	0.207	3900	0.296
1500	0.226	4200	0.301
1800	0.239	4500	0.303
2100	0.252	4800	0.305
2400	0.263	5100	0.309
2700	0.272	5400	0.311
3000	0.279	5700	0.311
3300	0.286	6000	0.312
3600	0.292		

SOLUTION D4B(2Ac)

$$(Pd) = 0.000327 \text{ M} ; (Cl^-) = 0.90 \text{ M} ; (NH_4^+) = 0.10 \text{ M}$$

Time (Sec)	Absorbance	Time (Sec)	Absorbance
300	0.213	3300	0.442
600	0.254	3600	
900	0.290	3900	0.459
1200	0.321	4200	0.466
1500	0.347	4500	0.469
1800	0.371	4800	0.474
2100	0.390	5100	0.478
2400	0.407	5400	0.479
2700	0.421	5700	0.481
3000	0.433	6000	0.482

Solution D4B($\frac{1}{2}$ Ac)

$$(Pd) = 0.000302 \text{ M} ; (Cl^-) = 0.90 \text{ M} ; (NH_4^+) = 0.10 \text{ M}$$

Time (Sec)	Absorbance	Time (Sec)	Absorbance
300	0.204	3300	0.440
600	0.245	3600	0.449
900	0.282	3900	0.458
1200	0.312	4200	
1500	0.339	4500	
1800	0.362	4800	0.473
2100	0.384	5100	0.478
2400	0.401	5400	0.481
2700	0.417	5700	0.485
3000	0.429	6000	0.487

Solution D4C

$$(Pd) = 0.000330 \text{ M} ; (Cl^-) = 0.80 \text{ M} ; (NH_4^+) = 0.20 \text{ M}$$

Time (Sec)	Absorbance	Time (Sec)	Absorbance
150	0.208	1650	0.418
300	0.249	1800	0.422
450	0.283	1950	0.427
600	0.313	2100	0.431
750	0.336	2250	0.432
900	0.356	2400	0.434
1050	0.372	2550	0.434
1200	0.387	2700	0.434
1350	0.400	2850	0.434
1500	0.409	3000	0.434

Solution D5C

$(\text{Pd}) = 0.000200 \text{ M}$; $(\text{Cl}^-) = 0.80 \text{ M}$; $(\text{NH}_4^+) = 0.20 \text{ M}$

Time	Absorbance	Time	Absorbance
150	0.140	1650	0.274
300	0.167	1800	0.277
450	0.191	1950	0.279
600	0.208	2100	0.280
750	0.224	2250	0.281
900	0.238	2400	0.282
1050	0.247	2550	0.282
1200	0.257	2700	0.281
1350	0.264	2850	0.281
1500	0.269	3000	0.279

Solution D5C0.7

$(\text{Pd}) = 0.000414 \text{ M}$; $(\text{Cl}^-) = 0.70 \text{ M}$; $(\text{NH}_4^+) = 0.20 \text{ M}$

Time	Absorbance	Time	Absorbance
180	0.322	1080	0.534
270	0.356	1170	0.547
360	0.386	1260	0.555
450	0.413	1350	0.563
540	0.436	1440	0.571
630	0.457	1530	0.579
720	0.476	1620	0.581
810	0.494	1710	0.588
900	0.509	1800	0.591
990	0.523		

Solution D5C0.5

$(\text{Pd}) = 0.000442 \text{ M}$; $(\text{Cl}^-) = 0.50 \text{ M}$; $(\text{NH}_4^+) = 0.20 \text{ M}$

Time	Absorbance	Time	Absorbance
90	0.301	990	0.542
180	0.342	1080	0.549
270	0.386	1170	0.556
360	0.420	1260	0.560
450	0.445	1350	0.563
540	0.469	1440	0.566
630	0.488	1530	0.568
720	0.505	1620	0.570
810	0.519	1710	0.569
900	0.531	1800	0.567

Solution D4D (I)

(Pd) = 0.000328 M ; (Cl⁻) = 0.85 M ; (NH₄⁺) = 0.15 M

Time	Absorbance	Time	Absorbance
150	0.213	2700	0.473
300	0.248	2850	
450	0.277	3000	0.481
600	0.305	3150	0.483
750	0.329	3300	0.484
900	0.351	3450	0.488
1050	0.369	3600	0.489
1200	0.386	3750	0.489
1350	0.402	3900	0.490
1500		4200	0.490
1650	0.428	4500	0.490
1800	0.436	4800	0.489
1950	0.444	5100	0.488
2100	0.452	5400	0.486
2250	0.459	5700	0.483
2400	0.463	6000	0.481
2550	0.468		

Solution D4D (II)

(Pd) = 0.000325 M ; (Cl⁻) = 0.85 M ; (NH₄⁺) = 0.15 M

Time	Absorbance	Time	Absorbance
150	0.205	2250	0.442
300	0.237	2400	0.449
450	0.267	2550	0.453
600	0.292	2700	0.458
750	0.314	2850	0.461
900	0.335	3000	0.464
1050	0.354	3150	0.468
1200	0.369	3300	0.470
1350	0.384	3450	0.471
1500	0.397	3600	0.473
1650	0.408	3750	0.473
1800	0.418	3950	0.473
1950	0.427		
2100	0.435		

Solution D5D0.7

(Pd) = 0.000445 M ; (Cl⁻) = 0.70 M ; (NH₄⁺) = 0.15 M

Time	Absorbance	Time	Absorbance
150	0.306	1650	0.603
300	0.356	1800	0.615
450	0.403	1950	0.627
600	0.441	2100	0.637
750	0.474	2250	0.643
900	0.504	2400	0.649
1050	0.531	2550	0.654
1200	0.554	2700	0.658
1350	0.573	2850	0.661
1500	0.591	3000	0.664

Solution D5D0.5

(Pd) = 0.000415 M ; (Cl⁻) = 0.50 M ; (NH₄⁺) = 0.15 M

Time	Absorbance	Time	Absorbance
90	0.294	990	0.530
180	0.331	1080	0.541
270	0.364	1170	0.552
360	0.395	1260	0.561
450	0.421	1350	0.570
540	0.444	1440	0.578
630	0.466	1530	0.585
720	0.485	1620	0.591
810	0.500	1710	0.594
900	0.515	1800	0.599

Solution D4E

$$(\text{Pd}) = 0.000255 \text{ M} ; \quad (\text{Cl}^-) = 0.98 \text{ M} ; \quad (\text{NH}_4^+) = 0.02 \text{ M}$$

Time	Absorbance	Time	Absorbance
300	0.159	5400	0.297
600	0.169	5700	0.303
900	0.179	6000	0.309
1200	0.188	6300	0.313
1500	0.197	6600	0.319
1800	0.206	6900	0.325
2100	0.214	7200	0.331
2400	0.223	7500	0.336
2700	0.230	7800	0.341
3000	0.238	8100	0.345
3300	0.246	8400	0.350
3600	0.256	8700	0.355
3900	0.263	9000	0.359
4200	0.270	9300	0.363
4500	0.277	9600	0.367
4800	0.284	9900	0.371
5100	0.290		

Solution D5F

$$(\text{Pd}) = 0.000441 \text{ M} ; \quad (\text{Cl}^-) = 1.0 \text{ M} ; \quad (\text{NH}_4^+) = 0.2 \text{ M}$$

Time	Absorbance	Time	Absorbance
300	0.206	3300	0.355
600	0.224	3600	0.366
900	0.241	3900	0.377
1200	0.258	4200	0.389
1500	0.274	4500	0.401
1800	0.289	4800	0.410
2100	0.304	5100	0.420
2400	0.318	5400	0.428
2700	0.330	5700	0.437
3000	0.343	6000	0.444

Solution E5A

(Pd) = 0.000481 M ; (Cl⁻) = 0.90 M ; (NH₄⁺) = 0.10 M

Time	Absorbance	Time	Absorbance
300	0.248	3900	0.526
600	0.287	4200	0.539
900	0.317	4500	0.552
1200	0.346	4800	0.565
1500	0.372	5100	0.574
1800	0.398	5400	0.582
2100	0.421	5700	0.591
2400	0.442	6000	0.600
2700	0.461	6300	0.607
3000	0.479	6600	0.614
3300	0.497	6900	0.618
3600	0.511	7200	0.622

Solution E4A0.7

(Pd) = 0.000360 M ; (Cl⁻) = 0.70 M ; (NH₄⁺) = 0.10 M

Time	Absorbance	Time	Absorbance
300	0.205	3900	0.418
600	0.234	4200	0.427
900	0.260	4500	0.435
1200	0.283	4800	0.443
1500	0.304	5100	0.450
1800	0.323	5400	0.456
2100	0.341	5700	0.461
2400	0.356	6000	0.466
2700	0.371	6300	0.471
3000	0.384	6600	0.475
3300	0.396	6900	0.479
3600	0.408	7200	0.481

Solution E3A0.5

(Pd) = 0.000298 M ; (Cl⁻) = 0.50 M ; (NH₄⁺) = 0.10 M

Time	Absorbance	Time	Absorbance
300	0.177	3000	0.319
600	0.202	3300	0.327
900	0.224	3600	0.334
1200	0.242	3900	0.340
1500	0.260	4200	0.345
1800	0.275	4500	0.350
2100	0.288	4800	0.354
2400	0.301	5100	0.358
2700	0.311	5400	0.360

Solution E5B

$(\text{Pd}) = 0.000442 \text{ M}$; $(\text{Cl}^-) = 1.0 \text{ M}$; $(\text{NH}_4^+) = 0.20 \text{ M}$

Time	Absorbance	Time	Absorbance
150	0.234	1650	0.447
300	0.262	1800	0.459
450	0.290	1950	0.471
600	0.315	2100	0.482
750	0.338	2250	0.491
900	0.360	2400	0.501
1050	0.380	2550	0.510
1200	0.398	2700	0.518
1350	0.417	2850	0.524
1500	0.432	3000	0.531

Solution E5B0.7

$(\text{Pd}) = 0.000447 \text{ M}$; $(\text{Cl}^-) = 0.70 \text{ M}$; $(\text{NH}_4^+) = 0.20 \text{ M}$

Time	Absorbance	Time	Absorbance
150	0.241	1650	0.472
300	0.276	1800	0.483
450	0.309	1950	0.494
600	0.339	2100	0.502
750	0.363	2250	0.511
900	0.386	2400	0.520
1050	0.410	2550	0.528
1200	0.428	2700	0.532
1350	0.443	2850	0.536
1500	0.459	3000	0.541

Solution E5B0.5

$(\text{Pd}) = 0.000455 \text{ M}$; $(\text{Cl}^-) = 0.50 \text{ M}$; $(\text{NH}_4^+) = 0.20 \text{ M}$

Time	Absorbance	Time	Absorbance
150	0.260	1500	0.484
300	0.304	1650	0.495
450	0.339	1800	0.502
600	0.371	1950	0.511
750	0.399	2100	0.519
900	0.421	2250	0.521
1050	0.441	2400	0.528
1200	0.458	2550	0.530
1350	0.471	2700	0.532

Solution E5C

(Pd) = 0.000407 M ; (Cl⁻) 1.0 M ; (NH₄⁺) = 0.15 M

Time	Absorbance	Time	Absorbance
150	0.232	1650	0.430
300	0.258	1800	0.442
450	0.284	1950	0.455
600	0.305	2100	0.467
750	0.327	2250	0.478
900	0.346	2400	0.488
1050	0.366	2550	0.496
1200	0.384	2700	0.504
1350	0.402	2850	0.511
1500	0.418	3000	0.519

Solution E5C0.7

(Pd) = 0.000455 M ; (Cl⁻) = 0.70 M ; (NH₄⁺) = 0.15 M

Time	Absorbance	Time	Absorbance
150	0.270	1650	0.498
300	0.303	1800	0.511
450	0.332	1950	0.525
600	0.358	2100	0.536
750	0.383	2250	0.547
900	0.407	2400	0.557
1050	0.428	2550	0.564
1200	0.448	2700	0.572
1350	0.465	2850	0.580
1500	0.482	3000	0.591

Solution E5C0.5

(Pd) = 0.000454 M ; (Cl⁻) = 0.50 M ; (NH₄⁺) = 0.15 M

Time	Absorbance	Time	Absorbance
150	0.269	1650	0.474
300	0.302	1800	0.485
450	0.331	1950	0.493
600	0.355	2100	0.503
750	0.376	2250	0.512
900	0.399	2400	0.520
1050	0.418	2550	0.527
1200	0.434	2700	0.531
1350	0.449	2850	0.536
1500	0.461	3000	0.541

Solution G5C

(Pd) = 0.000385 $\underline{\text{M}}$; (Cl⁻) = 1.0 $\underline{\text{M}}$; (NH₄⁺) = 0.2 $\underline{\text{M}}$

Time	Absorbance	Time	Absorbance
120	0.445	3120	0.534
240	0.469	3240	0.530
360	0.488	3360	0.529
480	0.501	3480	0.525
600	0.511	3600	0.522
720	0.521	3720	0.519
840	0.530	3840	0.514
960	0.537	3960	0.510
1080	0.540	4080	0.508
1200	0.544	4200	0.503
1320	0.548	4320	0.500
1440	0.550	4440	0.497
1560	0.552	4560	0.494
1680		4680	0.490
1800	0.552	4800	0.487
1920	0.553	4920	0.484
2040	0.553	5040	
2160		5160	0.477
2280	0.551	5280	0.474
2400	0.550	5400	0.471
2520	0.548	5520	0.468
2640	0.545	5640	0.465
2760	0.542	5760	0.461
2880	0.540	5880	0.460
3000	0.538	6000	0.457

Solution G5C0.75

(Pd) = 0.000405 $\underline{\text{M}}$; (Cl⁻) = 0.75 ; (NH₄⁺) = 0.2

Time	Absorbance	Time	Absorbance
150	0.413	3150	0.407
360	0.441	3300	0.401
450	0.446	3450	0.394
600	0.454	3600	0.389
750	0.457	3750	0.385
900	0.461	3900	
1050	0.460	4050	0.376
1200	0.459	4200	0.370
1350	0.459	4350	
1500	0.455	4500	0.364
1650	0.452	4650	0.360
1800	0.449	4800	0.354
1950	0.447	4950	0.349
2100	0.442	5100	0.345
2250	0.438	5250	0.342
2400	0.432	5400	0.338
2550	0.428	5550	0.335
2700	0.422	5700	0.331
2850	0.418	5850	0.329
3000	0.411	6000	0.326

Solution G5A0.5

(Pd) = 0.000436 M ; (Cl⁻) = 0.50 M ; (NH₄⁺) = 0.10 M

Time	Absorbance	Time	Absorbance
150	0.434	3150	0.492
300	0.455	3300	0.489
450	0.468	3450	0.487
600	0.474	3600	0.484
750	0.482	3750	0.481
900	0.489	3900	0.478
1050	0.501	4050	0.474
1200	0.502	4200	0.472
1350	0.502	4350	0.469
1560	0.502	4500	0.466
1650	0.502	4650	
1800	0.502	4800	0.460
1950	0.502	4950	0.457
2100	0.502	5100	0.453
2250	0.502	5250	0.451
2400		5400	0.448
2550	0.501	5550	0.445
2700	0.500	5700	0.441
2850	0.498	5850	0.438
3000	0.495	6000	0.435

APPENDIX B

Program KINET was written in FORTRAN IV language and executed on the Naval Postgraduate School IBM System 360 digital computer.

PROGRAM KINET

THIS PROGRAM

- 1) COMPUTES DA/DT AT EACH VALUE OF A EXCEPT THE FIRST AND LAST
- 2) PLOTS THE COMPUTED VALUES VERSUS A
- 3) COMPUTES THE BEST FIT STRAIGHT LINE THRU THE POINTS, INCLUDING STANDARD DEVIATIONS FOR BOTH SLOPE AND INTERCEPT
- 4) PLOTS THE COMPUTED LINE ON THE POINT PLOT
- 5) PRINTS THE LINE EQUATION, RATE CONSTANT IN RECIPROCAL SECONDS, ITS' STANDARD DEVIATION, INFINITY VALUE OF ABSORBANCE, AND ITS' STANDARD DEVIATION

INPUT REQUIREMENTS

FORMAT 1

L = NUMBER OF ABSORBANCE VALUES
T = TWICE THE ABSORBANCE SAMPLING INTERVAL IN MINUTES

FORMAT 2

A = ABSORBANCE VALUES

```
IMPLICIT REAL*8(A-F,O-Z)
DIMENSION V(50), W(50), X(50), Y(50), Z(50), A(50),
18(50), C(2,2), D(2,2), SDEVPR(2,2), G(50), H(50)
1 FORMAT (I6,F6.0)
2 FORMAT (8F8.4)
3 FORMAT (1H0,5X,'LINE EQUATION IS',5X,'DA/DT = ',
11PD13.5,' + ',1PD13.5,2X,'A', 5X,
2'STANDARD DEVIATION = ',1PD13.5)
6 FORMAT (1H0,20X,'K = ',1PD13.5,5X,'A INFINITY = ',
11PD13.5//15X,'STD DEV = ',1PD13.5,8X,'STD DEV = ',
21PD13.5)
101 FORMAT (//5X,'MATRIX SINGULAR'//)
```

```

109 FORMAT(/5X,'THE INVERSE OF THE COEFFICIENT MATRIX IS')
112 FORMAT (//10X,1PD13.5,10X,1PD13.5//10X,1PD13.5,10X,
113 1PD13.5)
900 READ (5,1) L,T
DO 10 I = 1,50
  A(I) = 0.0
  B(I) = 0.0
  V(I) = 0.0
  W(I) = 0.0
  X(I) = 0.0
  Y(I) = 0.0
  Z(I) = 0.0
10 CONTINUE
  SUMV = 0.0
  SUMW = 0.0
  SUMX = 0.0
  SUMY = 0.0
  SUMZ = 0.0
  READ (5,2) (A(I),I = 1,L)
  M = L - 1
  DO 20 I = 2,M
    X(I-1) = A(I)
20 CONTINUE
  DO 30 I = 3,L
    B(I-2) = A(I)
30 CONTINUE
  N = L - 2
  DO 40 I = 1,N
    Y(I) = (B(I) - A(I))/T
40 CONTINUE
  DO 50 I = 1,L
    V(I) = Y(I)**2.0
    W(I) = X(I)**2.0
    Z(I) = X(I)*Y(I)
    SUMV = SUMV + V(I)
    SUMW = SUMW + W(I)
    SUMX = SUMX + X(I)
    SUMY = SUMY + Y(I)
    SUMZ = SUMZ + Z(I)
50 CONTINUE
  XBAR = SUMX/N
  YBAR = SUMY/N
  SLOPE = (SUMZ - (XBAR*SUMY))/(SUMW - (SUMX*XBAR))
  ENT = YBAR - (SLOPE * XBAR)
  SNUM = (SUMZ - (XBAR * SUMY)) * (SUMZ - (XBAR * SUMY))

```

```

SDEV = DSQRT(((SUMV-(SUMY*YBAR))-(SNUM/
1(SUMW-(SUMX*XBAR))))/(L-2))
WRITE (6,3) ENT, SLOPE, SDEV
SLOPES = DABS(SLOPE/60.0)
AINF = DABS(ENT/SLOPE)
Q = N
C(1,1) = SUMW
C(1,2) = SUMX
C(2,1) = SUMX
C(2,2) = Q
CALL GAUSS3 (2,1.00D-30,C,D,ITEST)

```

GAUSS3 COMPUTES THE INVERSE OF THE SQUARE MATRIX

```

      SUMW      SUMX
      SUMX      N

```

```

      IF (ITEST - 1) 100,110,100
110 WRITE (6,109)
      DO 111 I = 1,2
111 WRITE (6,112) (D(I,J), J = 1,2)
      SDEVSQ = SDEV**2.0
      DO 120 I = 1,2
      DO 130 J = 1,2
      SDEVPR(I,J) = SDEVSQ * D(I,J)
130 CONTINUE
120 CONTINUE
      SDEVSL = DSQRT(SDEVPR(1,1))/60.0
      SDEVIN = DSQRT(SDEVPR(2,2))
      WRITE (6,6) SLOPES, AINF, SDEVSL, SDEVIN
      IF (ITEST-1) 100,140,100
100 WRITE (6,101)
      GO TO 900
140 IF (L.GT.30) L = 30
      REAL LABEL /4H /
      REAL*8 ITITLE(12)
1/' JOB KINET MONK,W.W. BOX 77
2 DA/DT VS. A ,/
      M = 1
      IT = 1
55 DO 150 I = 1,L
      G(I) = X(I)

```

```

      H(I) = Y(I)
150 CONTINUE
      CALL DRAW (L,G,H,M,IT,LABEL,ITITLE,0,0,0,0,0,0,8,10,1,
1(LAST)

```

C
C
C
C
C

```

      DRAW PLOTS BOTH THE COMPUTED POINTS AND THE BEST FIT
      LINE ON DA/DT VERSUS A AXES

```

```

      IF(M.EQ.3) GO TO 900
      M = 3
      IT = 0
      Y(1) = 0.0
      DO 60 I = 1,L
      X(I) = (Y(I)/SLOPE) + AINF
      Y(I+1) = Y(I) + 0.002
60 CONTINUE
      GO TO 55
      END

```

```

      SUBROUTINE GAUSS3(N,EP,A,X,KER)
      IMPLICIT REAL*8(A-H,O-Z)
      DIMENSION A(2,2), X(2,2)
      DO 1 I=1,N
      DO 1 J=1,N
1 X(I,J)=0.0
      DO 2 K=1,N
2 X(K,K)=1.0
10 DO 34 L=1,N
      KP=0
      Z=0.0
      DO 12 K=L,N
      IF(Z-DABS(A(K,L))) 11,12,12
11 Z=DABS(A(K,L))
      KP=K
12 CONTINUE
      IF(L-KP)13,20,20
13 DO 14 J=L,N
      Z=A(L,J)
      A(L,J)=A(KP,J)

```

```

14 A(KP,J)=Z
   DO 15 J=1,N
     Z=X(L,J)
     X(L,J)=X(KP,J)
15 X(KP,J)=Z
20 IF(DABS(A(L,L))-EP) 50,50,30
30 IF(L=N)31,34,34
31 LP1=L+1
   DO 36 K=LP1,N
     IF(A(K,L))32,36,32
32 RATIO=A(K,L)/A(L,L)
   DO 33 J=LP1,N
33 A(K,J)=A(K,J)-RATIO*A(L,J)
   DO 35 J=1,N
35 X(K,J)=X(K,J)-RATIO*X(L,J)
36 CONTINUE
34 CONTINUE
40 DO 43 I=1,N
   II=N+1-I
   DO 43 J=1,N
     S=0.0
     IF(II=N)41,43,43
41 IIP1=II+1
   DO 42 K=IIP1,N
42 S=S+A(II,K)*X(K,J)
43 X(II,J)=(X(II,J)-S)/A(II,II)
   KER=1
   RETURN
50 KER=2
   RETURN
END

```

INITIAL DISTRIBUTION LIST

	No. Copies
1. Defense Documentation Center Cameron Station Alexandria, Virginia 22314	20
2. Library Naval Postgraduate School Monterey, California, 93940	2
3. Commander Naval Ordnance Systems Command Hqs. Navy Department Washington, D. C., 20360	1
4. Professor Richard A. Reinhardt Department of Material Science and Chemistry Naval Postgraduate School Monterey, California 93940	1
5. LT William W. Monk 501 Coral Place Corpus Christi, Texas, 78411	1
6. Chairman, Department of Material Science and Chemistry Naval Postgraduate School Monterey, California 93940	3
7. LCDR Robert K. Sparkes, RCN Staff Director of Weapons Systems Canadian Services Headquarters Cartier Square, Ottawa, Canada	1

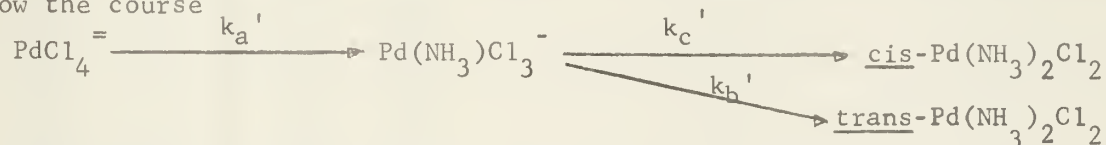
DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Naval Postgraduate School Monterey, California, 93940		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE Kinetics of Ammonia Substitution Into Tetrachloropalladate (II) Ion			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Thesis			
5. AUTHOR(S) (First name, middle initial, last name) Monk, William Wade			
6. REPORT DATE June 1968	7a. TOTAL NO. OF PAGES 61	7b. NO. OF REFS 13	
8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)		
b. PROJECT NO.			
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
d.			
10. DISTRIBUTION STATEMENT This document is classified "Secret" and is controlled by the Naval Postgraduate School. No other distribution is authorized without the approval of the Naval Postgraduate School.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Naval Postgraduate School Monterey, California, 93940	

13. ABSTRACT

The kinetics of ammonia substitution into tetrachloropalladate (II) ion were studied by ultraviolet spectroscopy. The reactions in aqueous solution follow the course



Each pseudo-first-order rate constant was found to obey the two-term rate law

$$k' = k_1 \frac{(\text{NH}_3)}{1 + (\text{Cl}^-)} + k_2 (\text{NH}_3)$$

Values found at 30°C and $\mu = 1$ are $k_{a1} = 89.8 \text{ sec}^{-1}$, $k_{a2} = 31.3 \text{ M}^{-1} \text{ sec}^{-1}$, $k_{b1} = 12.5 \text{ sec}^{-1}$, and $k_{b2} = 6.5 \text{ M}^{-1} \text{ sec}^{-1}$. Values estimated for the rapid step leading to $\text{cis-Pd}(\text{NH}_3)_2\text{Cl}_2$ are $k_{c1} = 630 \text{ sec}^{-1}$ and $k_{c2} = 220 \text{ M}^{-1} \text{ sec}^{-1}$.

Activation parameters of the first step are calculated.

The trans and cis effects are discussed.

KEY WORDS

[illegible]



shen8672

DUDLEY KNOX LIBRARY



3 2768 00416407 9

2/68 UUZ U4/U3 /

DUDLEY KNOX LIBRARY